

Changes in the Ta/Nb Ratio in Successively Formed Differentiates of Granite Melt (Calculations Based on Experimental Data)

Ya.O. Alferyeva[✉], E.N. Gramenitskii, T.I. Shchekina

Lomonosov Moscow State University, Leninskie Gory, Moscow, 119991, Russia

Received 25 July 2018; accepted 5 February 2019

Abstract—Based on experimental data ($T = 650\text{--}800\text{ }^{\circ}\text{C}$, $P = 1\text{--}2\text{ kbar}$) on the solubility of columbite and tantalite in silicate melt and on the distribution of Ta and Nb among coexisting silicate melt, aqueous fluid, and aluminum fluoride melt, we calculated a possible change in the Ta/Nb indicator ratio in residual deeply differentiated granite melts. The Clarke values of these metals in acid rocks of the Earth's crust were taken as their initial contents. The calculations were made by the mass balance method. It is shown that the separation of fluid in the closed magmatic system rock-forming minerals–silicate melt–water can lead to an approximately twice increase in Ta/Nb in the residual melt as compared with the initial Clarke value. In the system rock-forming minerals–silicate melt–aluminum fluoride melt with the initial content of fluorine close to that in biotite granites, the Ta/Nb ratio in the residual melt can increase to ~ 1 . Successive crystallization of minerals of the isomorphic columbite–tantalite series can lead to $\text{Ta/Nb} > 2$ in the residual melt. Crystallization of biotite causes a significant increase in Ta/Nb and prevents the accumulation of these metals in the residual silicate melt.

Keywords: rare-metal granites, Ta and Nb deposits, columbite, tantalite, Ta/Nb indicator ratio

INTRODUCTION

Tantalum and niobium are heavy lithophile metals. Their position in the same group of the periodic table of elements determines their similar properties and similar behavior in geologic processes. These elements have close atomic radii and ionization potentials and therefore coexist in minerals and rocks. During crystallization differentiation, Ta and Nb accumulate in residual magmatic melts. Their contents reach a maximum in the most deeply differentiated rocks.

The Clarke value of Ta in the Earth's crust is approximately ten times lower than the Clarke value of Nb (Solodov, 1978). In some cases, the empirically established difference between the Ta/Nb ratio in the object and the ratio of the Clarke values of these elements is considerable and is used as a geochemical indicator. For example, Ta/Nb in Nb deposits in carbonatites reaches 0.02. In granitoids, depending on their geochemical type, the average Ta/Nb ratio varies from 0.05 to 0.5 (Tauson, 1977). The most evolved varieties of Li–F granites, which are the differentiation products of granitoids of normal alkalinity, have close contents of Ta and Nb; sometimes, Ta even prevails (Kovalenko, 1977; Beskin, 2014).

The Orlovka and Etyka deposits in eastern Transbaikalia are typical examples of such Li–F deposits. Biotite granites of the Kukul'bei Group, which are parent rocks of rare-met-

al Li–F granites of these deposits, contain 5×10^{-4} wt.% Ta and 2×10^{-3} wt.% Nb (Syrityso et al., 2001). These contents are just slightly higher than the Clarke values of Ta and Nb in the acid rocks of the Earth's crust. Younger differentiates (topaz-containing microcline–albite granites) are richer in these elements: Ta = 5×10^{-4} and Nb = 2×10^{-3} wt.% (Zarasky et al., 2009). Some of the most differentiated rock varieties in the apical parts of the massifs contain 4×10^{-2} wt.% Ta and 3×10^{-2} wt.% Nb (Badanina et al., 2010), i.e., dozens of times more than the initial Clarke values. An increase in the contents of these metals in successively formed magma differentiates is accompanied by an increase in the Ta/Nb ratio: 0.25, 0.7, and 1.3.

A similar increase in the Ta/Nb ratio is also observed in the successively formed Erzgebirge (Germany) granite differentiates (Forster, 1998), in rapakivi granite complexes with topaz- or cryolite-containing granites as late differentiates (e.g., in the Pitinga province in Brazil) (Lenharo, 2003), in the topaz-containing granites of the Kymi stock, associated with the Vyborg rapakivi granites (Haapala and Lukkari, 2005), and of the Eurajoki stock (Haapala, 1997), etc. Some alkaline rocks with a high degree of melt differentiation show a gradual regular change in the Ta/Nb ratio (e.g., at the Zashikhin and Ulugtanzenk deposits) (Beskin, 2014). Many pegmatite varieties, which are late differentiates of magmatic melt, also have high Ta/Nb ratios (Cerny and Er-cit, 1985).

In this work we consider normal and subalkalic acid rocks, plumasitic or having the mole ratio $\text{Al}_2\text{O}_3/(\text{Na}_2\text{O} +$

[✉] Corresponding author.

E-mail address: YanaAlf@ya.ru (Ya.O. Alferyeva)

$K_2O) = A/NK \approx 1$. Topaz- and/or cryolite-containing high-F granites are their most differentiated varieties.

STATEMENT OF THE PROBLEM

An increase in the contents of Ta and Nb in acid igneous rocks is related to crystallization differentiation. Genesis of rock-forming and accessory minerals, formation of an aqueous fluid at the magmatic stage, or separation of another liquid phase from a silicate melt through liquation can lead to an increase in the contents of Ta and Nb in the residual melt, up to the solubility products of the Ta–Nb phases. The same processes seem to cause an increase in the Ta/Nb ratio in successively formed magma differentiates.

(1) Present in low contents in the melt, Ta and Nb are distributed between the melt L and the coexisting phases X. The behavior of Ta and Nb is described by the partition coefficients $K_{pMe} = C_{Me}^X/C_{Me}^L$, where C_{Me}^X and C_{Me}^L are the contents of metal (wt.%) in the phase X and in the silicate melt, respectively. An increase in C_{Ta}^L/C_{Nb}^L in the residual melt is achieved if K_{pNb} is greater than K_{pTa} .

The possible phases X are as follows: (1) silicate or other minerals (S) with Ta and Nb impurities; (2) aqueous fluid (fl); (3) salt, water–silicate, or any other liquid phases (B) produced by the liquid immiscibility mechanism, which are called salt melt, melt–brine, fluid melt, “heavy phase”, LF, fluoride–calcium melt, brine, etc. (Fersman, 1960; Dolomanova, 1966; Ryabchikov and Hamilton, 1971; Kogarko and Krigman, 1981; Gramenitskii and Shchekina, 1993; Veksler, 2002; Gramenitskii et al., 2005; Reif, 2009; Peretyazhko and Savina, 2010; Shchekina et al., 2013; Peretyazhko et al., 2011).

(2) Crystallization differentiation increases the contents of Ta and Nb in the melt, up to the solubility product of their own phases, e.g., Ta niobates. An increase in C_{Ta}^L/C_{Nb}^L in the residual melt becomes possible in the case of the earlier crystallization of essentially niobium mineral and the formation of an essentially tantalum analog at later stages.

Based on experimental data and using mathematical modeling methods, we attempt to determine which of the above processes lead to the accumulation of Ta relative to Nb in successively formed differentiates of magmatic melt.

To solve this problem, we studied the following model systems:

1. Silicate melt and phases with Ta and Nb impurities:
 - 1.1. L–S, melt and crystalline phases,
 - 1.2. L–fl, melt and aqueous fluid (closed system),
 - 1.3. L–B, silicate melt and liquid phase immiscible with it.
2. Silicate melt and essentially Ta–Nb ore phases within the tantalite–columbite series (L–TN).

To compare the numerical results, we used the following parameters:

- (1) C_{Ta}^L/C_{Nb}^L in the residual melt, whose mass M_L is equal to 0.0001 of the mass of the primary melt, M_{L_0} .
- (2) The contents of metals in the residual melt, C_{Ta}^L and C_{Nb}^L .

NUMERICAL-MODELING TECHNIQUE

1.1. Silicate melt and crystalline phases with Ta and Nb impurities (L–S). Let us consider a closed model system under conditions of ideal fractional crystallization (Bowen, 1934; Maaloe, 1976; Ariskin and Barmina, 2000), in which minerals (S), with one of them (1S) containing Nb and Ta impurities, crystallize from aluminosilicate melt L_0 with Clarke contents of Ta and Nb. At any crystallization step (N), the mass of metal in the produced crystalline substance S ($m_{Me}^{S(N)}$) is equal to the mass of metal in the phase 1S ($m_{Me}^{1S(N)}$).

Since the amount of substance in the system does not change, the sum of the masses of metal in the elementary volume of the crystalline substance ($m_{Me}^{S(N)} = m_{Me}^{1S(N)}$) and of the metal in the equilibrium melt ($m_{Me}^{L(N)}$) at any crystallization step is equal to the mass of the metal in the melt at the previous step ($m_{Me}^{L(N-1)}$):

$$m_{Me}^{L(N-1)} = m_{Me}^{L(N)} + m_{Me}^{1S(N)}.$$

The mass of the metal in any phase X is equal to

$$m_{Me}^X = C_{Me}^X M_X, \quad (1)$$

where M_X is the mass of this phase. The mass fraction of the phase 1S is h ($M_{1S} = hM_S$ at $0 \leq h \leq 1$). Substituting the content of the metal in the crystalline substance by the measured value of $K_{pMe} = C_{Me}^{1S}/C_{Me}^L$, we obtain

$$C_{Me}^{L(N-1)} M_{L(N-1)} = C_{Me}^{L(N)} M_{L(N)} + K_{pMe} C_{Me}^{L(N)} h M_{S(N)}.$$

Since $M_{S(N)} = M_{L(N-1)} - M_{L(N)}$, then

$$C_{Me}^{L(N)} = \frac{C_{Me}^{L(N-1)} M_{L(N-1)}}{M_{L(N)} (1 - hK_{pMe}) + M_{L(N-1)} hK_{pMe}}. \quad (2)$$

Expression (2) is the dependence of the metal content in the residual melt, C_{Me}^L , on the amount of this melt, M_L . In the limiting form ($M_{L(N-1)} - M_{L(N)} \rightarrow 0$), this expression is identical to the equations obtained by Ariskin and Barmina (2000).

In the case of a regular change in the amount of the phase 1S in the elementary volume S during crystallization, the coefficient h can be specified as a function of the mass of the residual melt, M_L .

1.2. Silicate melt and aqueous fluid (L–fl). Fluid can appear in the magmatic system as a result of retrograde boiling of a crystallizing melt, decompression, or from external sources. Here we consider only the first variant. The fluid is highly mobile and lowly viscous and thus has specific features that must be taken into account on calculations.

Let us consider a system in which the C_{Ta}^L/C_{Nb}^L ratio can change only under L–fl interaction. The primary melt L_0 has Clarke contents of Ta and Nb and is saturated with water. During crystallization of rock-forming minerals free of Ta

and Nb, the amount of the melt in the system decreases, and the fluid mass, C_{Ta}^L , and C_{Nb}^L increase.

If each elementary portion of the fluid is removed and does not interact with the system substance any longer (ideal fractionation), then the following equalities are valid at the differentiation step N :

$$\begin{aligned} m_{Me}^{L(N-1)} &= m_{Me}^{L(N)} + m_{Me}^{fl(N)} \\ m_{H_2O}^{L(N-1)} &= m_{H_2O}^{L(N)} + m_{H_2O}^{fl(N)}, \end{aligned} \quad (3)$$

where $m_{Me}^{fl(N)}$ and $m_{H_2O}^{fl(N)}$ are the masses of metal and water, respectively, in the elementary portion of the fluid produced at the step N .

Taking into account (1) and substituting the concentration of metal in the fluid by the measured values of $K_{pMe} = C_{Me}^{fl}/C_{Me}^L$, we obtain

$$\begin{aligned} C_{Me}^{L(N)} &= C_{Me}^{L(N-1)} \frac{M_{L(N-1)}}{M_{L(N)} + K_{pMe} M_{fl(N)}}, \\ M_{fl(N)} &= \frac{C_{H_2O}^{L(N-1)} M_{L(N-1)} - C_{H_2O}^{L(N)} M_{L(N)}}{C_{H_2O}^{fl(N)}}, \end{aligned} \quad (4)$$

where $C_{H_2O}^{L(N)}$ and $C_{H_2O}^{fl(N)}$ are the mass fractions of water in the residual melt and in the elementary volume of the fluid, respectively, at the step N .

As a result,

$$C_{Me}^{L(N)} = \frac{C_{H_2O}^{fl(N)} C_{Me}^{L(N-1)} M_{L(N-1)}}{M_{L(N)} (C_{H_2O}^{fl(N)} - K_{pMe} C_{H_2O}^{L(N)}) + K_{pMe} C_{H_2O}^{L(N-1)} M_{L(N-1)}}. \quad (5)$$

If the entire fluid produced during crystallization remains in the system and, being lowly viscous, comes to equilibrium with each new composition of the melt, then (3) can be written as

$$\begin{aligned} m_{Me}^{L_0} &= m_{Me}^{L(N)} + m_{Me}^{fl(1,2,\dots,N)}, \\ m_{H_2O}^{L_0} &= m_{H_2O}^{L(N)} + m_{H_2O}^{fl(1,2,\dots,N)}, \end{aligned}$$

where $m_{Me}^{fl(1,2,\dots,N)}$ and $m_{H_2O}^{fl(1,2,\dots,N)}$ are the masses of the metal and water, respectively, in the entire fluid produced before and at the step N . Taking $M_{L_0} = 1$ and following the calculation scheme as in (4), we obtain

$$C_{Me}^{L(N)} = \frac{C_{H_2O}^{fl(1,2,\dots,N)} C_{Me}^{L_0}}{M_{L(N)} (C_{H_2O}^{fl(1,2,\dots,N)} - K_{pMe} C_{H_2O}^{L(N)}) + K_{pMe} C_{H_2O}^{L_0}}. \quad (6)$$

Expressions (5) and (6) are the dependence of C_{Me}^L on the mass of the residual melt, M_L . In nature, only part of the fluid comes to equilibrium with the melt during crystallization. Therefore, (5) and (6) yield the limiting contents of metal in the residual melt during the L–fl interaction.

1.3. Silicate melt and liquid phase immiscible with it (L–B). As phase B, we take any liquid phase produced in

equilibrium with a deeply differentiated aluminosilicate melt by the liquid immiscibility mechanism. The shape of the immiscibility region and the position of critical curves can be different depending on the P – T conditions and the composition of the system (Valyashko, 1990). The proposed calculation method does not take into account changes in the phase state depending on the P – T conditions.

Let us consider a model system in which component Z necessary for the formation of liquid B accumulates, along with Ta and Nb, as a result of crystallization in the residual aluminosilicate melt. Under these P – T conditions and system composition, phase B forms when the content of component Z in the melt reaches a maximum. Distribution of Ta and Nb between the coexisting melts is described by the expression $K_{pMe} = C_{Me}^B/C_{Me}^L$.

Under fractionation or equilibrium coexistence of two melts, C_{Me}^L in the silicate melt will be determined (as in Section 1.2) as follows:

$$C_{Me}^{L(N)} = \frac{C_Z^{B(N)} C_{Me}^{L(N-1)} M_{L(N-1)}}{M_{L(N)} (C_Z^{B(N)} - K_{pMe} C_Z^{L(N)}) + K_{pMe} C_Z^{L(N-1)} M_{L(N-1)}}$$

or

$$C_{Me}^{L(N)} = \frac{C_Z^{B(1,2,\dots,N)} C_{Me}^{L_0}}{M_{L(N)} (C_Z^{B(1,2,\dots,N)} - K_{pMe} C_Z^{L(N)}) + K_{pMe} C_Z^{L_0}}, \quad (7)$$

where M_L is limited by the stability region of liquid B, $C_Z^{L_0}$ and $C_Z^{L(N)}$ are the contents of component Z in the primary melt and in the deeply differentiated silicate melt, respectively, $C_Z^{B(N)}$ is the content of Z in the elementary unit of liquid B, and $C_Z^{B(1,2,\dots,N)}$ is the content of Z in the total volume of liquid B.

2. Silicate melt and Ta–Nb ore phases (L–TN). We consider crystallization of Ta–Nb ore minerals by the example of the isomorphous columbite (Col)–tantalite (Tan) series.

Crystallization differentiation leads to an increase in the contents of Ta and Nb in the residual melt up to the solubility product of columbite–tantalite (Col–Tan), which is represented by a Fe-free end-member in this model and has general formula $MnTa_xNb_{2(1-x)}O_6$ ($0 \leq x \leq 1$). The content of MnO in the silicate melt is taken to be constant and equal to 0.2 wt.%, typical of granites.

The influence of Col–Tan crystallization on C_{Ta}^L/C_{Nb}^L can be estimated using special calculation algorithms (Ariskin and Barmina, 2000), experimentally determined solubility product (SP), and distribution coefficient K_d :

$$K_d = \frac{n_{Nb_2O_5}^{Col} n_{Ta_2O_5}^L}{n_{Nb_2O_5}^L n_{Ta_2O_5}^{Col}}, \quad (8)$$

where $n_{MeO}^{L,Col}$ is the molar concentration of oxide in the corresponding phase.

Coefficient K_d remains constant for ideal solid solutions. A limited amount of experimental data does not permit us to

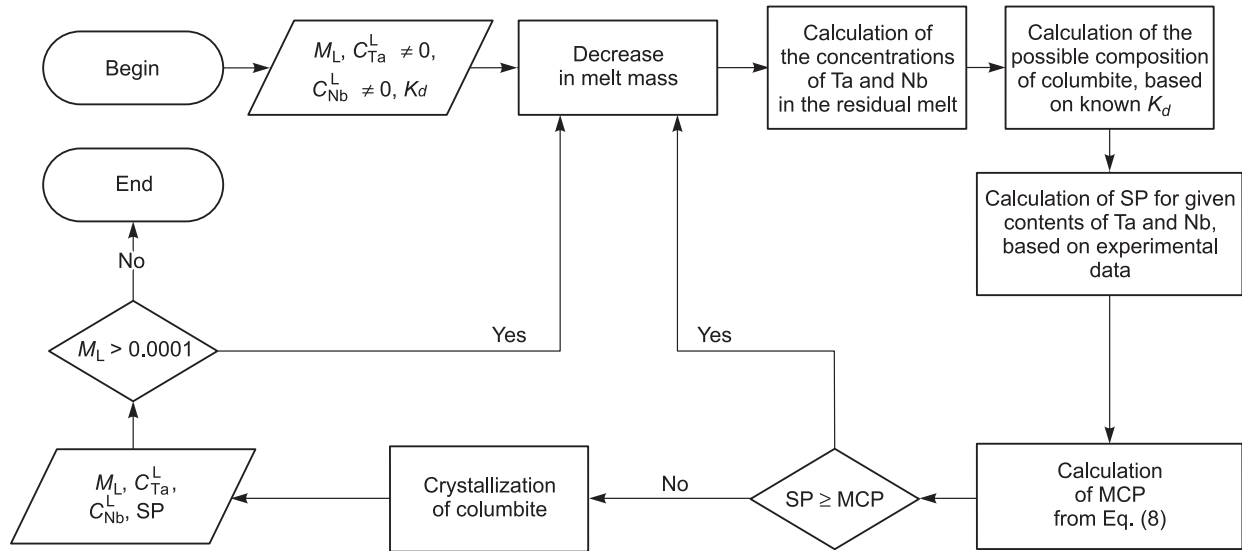


Fig. 1. Algorithm of calculation of C_{Ta}^L and C_{Nb}^L in the residual silicate melt during crystallization of minerals of the isomorphous columbite–tantanite series.

estimate the degree of ideality of the Col–Tan solution. However, based on the similar chemical and thermodynamic properties of Ta and Nb, we suggest that $K_d \approx \text{const}$ in the case of a minor change in the silicate melt composition and the approximately constant amount of Mn.

The equality of the experimentally obtained SP and the molar-concentration product (MCP) for $\text{MnTa}_{2x}\text{Nb}_{2(1-x)}\text{O}_6$, expressed as

$$\text{MCP} = n_{\text{MnO}}^L (n_{\text{Ta}_2\text{O}_5}^L)^x (n_{\text{Nb}_2\text{O}_5}^L)^{1-x}, \quad (9)$$

is the criterion for the beginning of crystallization of columbite in melt L.

The block scheme in Fig. 1 generally describes the calculation algorithm.

RESULTS AND DISCUSSION

Note that the above formulas are universal and can be used to estimate the contents of various trace elements under interaction of various phases. The numerical values obtained below are examples of calculation by these formulas and are not universal.

The Clarke values of Nb and Ta in acid rocks of the Earth’s crust are taken equal to $C_{Nb}^{L_0} = 2.0 \times 10^{-3}$ and $C_{Ta}^{L_0} = 3.5 \times 10^{-4}$ wt.% (Solovov, 1990).

1.1. Silicate melt and crystalline phases with Ta and Nb impurities (L–S). As an example, we consider a system with biotite as a crystalline phase (1S) containing Ta and Nb impurities (Nash and Crecraft, 1985; Acosta-Vigil et al., 2010).

In the ultimate case, when biotite is absent, $h = 0$ in (2), the C_{Ta}^L/C_{Nb}^L ratio remains constant, and the contents of Ta and Nb in the residual melt increase (Fig. 2). The L–S sys-

tem with $h = 0$ is a hypothetical case when Ta and Nb are not dispersed in crystalline or any other phases and accumulate in maximum possible contents in the residual melt. Under real conditions, the contents of Ta and Nb in the melt are limited by the formation of phases with Ta and Nb impurities and by the solubility limits of Ta–Nb minerals.

The coefficients of Ta and Nb partition between the acid melt and biotite are $K_{pTa} = 1.9\text{--}3.6$ and $K_{pNb} = 8.7\text{--}9.1$ (Nash and Crecraft, 1985; Acosta-Vigil et al., 2010). As shown in Fig. 2A, even 5 wt.% biotite contributes to a significant increase in C_{Ta}^L/C_{Nb}^L and deceleration of the accumulation of Ta and Nb in the residual melt. A constant 20 wt.% content of Bt ensures rapid increase in C_{Ta}^L/C_{Nb}^L , but the dispersion of metals in the crystalline material is so high that the accumulation of Nb in the residual melt becomes impossible.

In most of natural intrusive granite complexes, the content of mafic minerals significantly decreases from early to late intrusive phases. Below we qualitatively assess whether a decrease in the amount of biotite in successive portions of crystalline material can affect the above-obtained results.

We accept that the amount of biotite in the elementary crystallization volume depends linearly on the mass of the residual melt M_L and decreases from 5 or 20 wt.% in the first portions of crystalline substance to zero in the last ones. Figure 2B shows that with given parameters providing a gradual reduction in the “color index” of successive differentiates, biotite can cause an increase in C_{Ta}^L/C_{Nb}^L at the initial stages of crystallization and prevents the accumulation of these metals in the residual melt, although not so seriously as in the first case.

Strictly speaking, the amount of biotite in the elementary crystallization volume is not a function of the mass of the residual melt. It depends on the composition of the melt, the presence of fluid, etc. and differs significantly in different

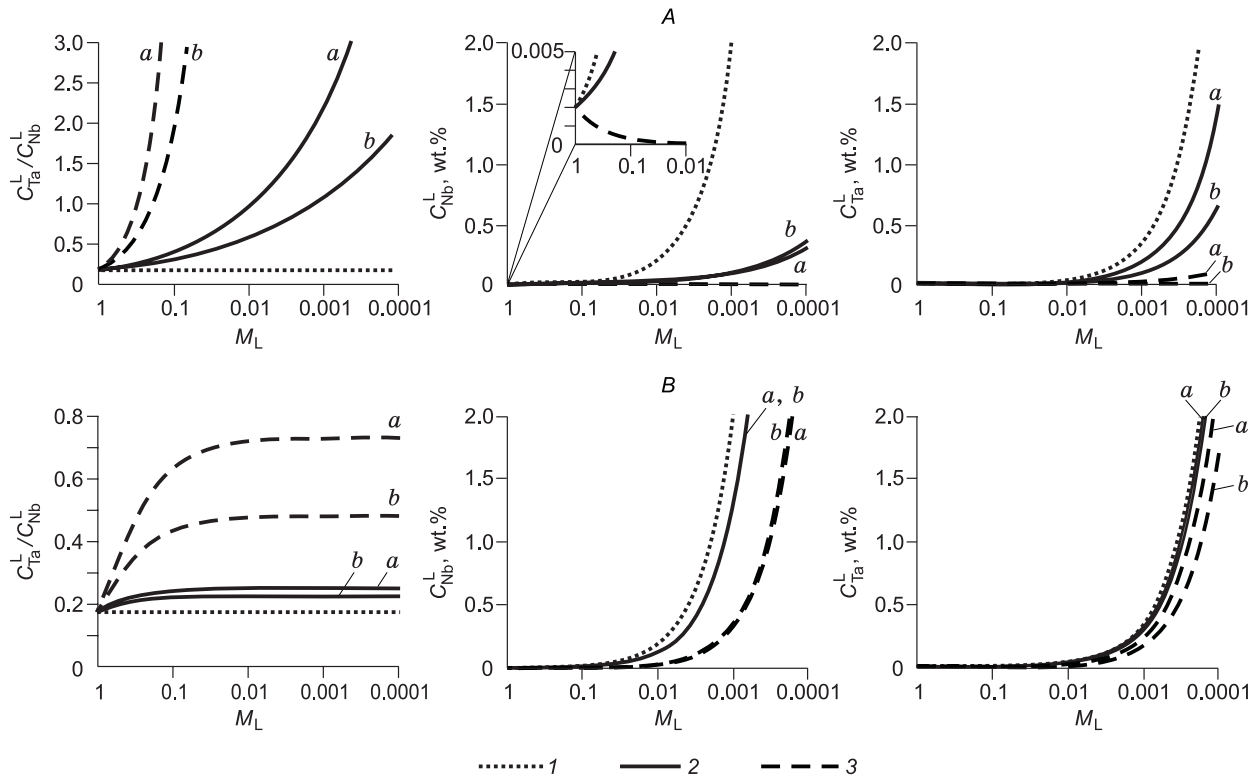


Fig. 2. Results of modeling in the system L–S by the example of the silicate–melt–biotite interaction. Changes in C_{Ta}^L/C_{Nb}^L and the contents of Ta and Nb in the residual melt depending on the content of biotite in the elementary crystallization volume: *A*, the content of biotite is constant throughout crystallization; *B*, the content of biotite linearly decreases to 0 wt.% in the final portions of melt. The initial content of biotite (wt.%): 1; 0; 2; 5; 3; 20. The curves were constructed based on experimental data: *a*, (Nash and Crecraft, 1985); *b*, (Acosta-Vigil et al., 2010).

natural systems. The simple linear dependence given here as an example does not exactly reflect the real changes in the biotite content in the crystallizing material but clearly demonstrates their significance. The change in the “color index” of the rock in passing from early to late differentiates must be taken into account when constructing mathematical models of ore-magmatic systems.

1.2. Silicate melt and aqueous fluid (L–fl). The values of K_{pMe} for F-containing high- and medium-plumasite granite systems were earlier obtained at 650–750 °C and 1 kbar under equilibrium of silicate melt and aqueous fluid (Chevychelov et al., 2005; Borodulin et al., 2009). The equilibrium is due to the redistribution of all components in the system between the melt and the fluid, i.e., the composition of the fluid depends seriously on the composition of the equilibrium melt. For such systems, K_{pTa} and K_{pNb} are within 0.001–0.006 and 0.003–0.01, respectively (Borodulin et al., 2009). In (5) and (6) we accept

$$C_{H_2O}^{fl(N)} \approx C_{H_2O}^{fl(1,2,\dots,N)} \approx 1.$$

Figure 3 presents the results of calculation of the L–fl interaction. Under ideal fractionation, the presence of fluid virtually does not influence the contents of Ta and Nb in the residual silicate melt. Within the model scale, these data coincide with the results of calculation in a fluid-free system.

The strongest influence of the fluid is observed in the absence of fractionation between L and fl, when all fluid separated from the melt remains in the system and comes to equilibrium with successively formed melt differentiates.

According to experimental data (Holtz et al., 1993; Webster et al., 2004; Baker and Alletti, 2012; Alferyeva et al., 2018), the solubility of water in silicate melt depends on the presence of impurities in the system. For example, at 1 kbar and ~800 °C, the presence of fluorine can increase the solubility of water in acid melt from 4 to 7–8 wt.%. A still greater increase in water solubility might be expected in successively formed differentiates of natural melts.

In a closed system, however, the amount of produced magmatogene fluid is determined mostly by the total content of the corresponding volatile component (in our case, water) and its solubility in the primary melt.

In the equilibrium system with a gradual increase in water solubility from 4 to 15 wt.%, the C_{Ta}^L/C_{Nb}^L ratio in the residual melt can increase approximately twice (Fig. 3). The same result was obtained with the constant solubility of water in melt, equal to 4 wt.%. At the initial high (10 wt.%) water solubility, the L–fl interaction is somewhat stronger. In this case, the C_{Ta}^L/C_{Nb}^L ratio increases 2.5 times. However, such water solubility seems to be unreal in the primary granite melts with a low or medium degree of crystallization differentiation.

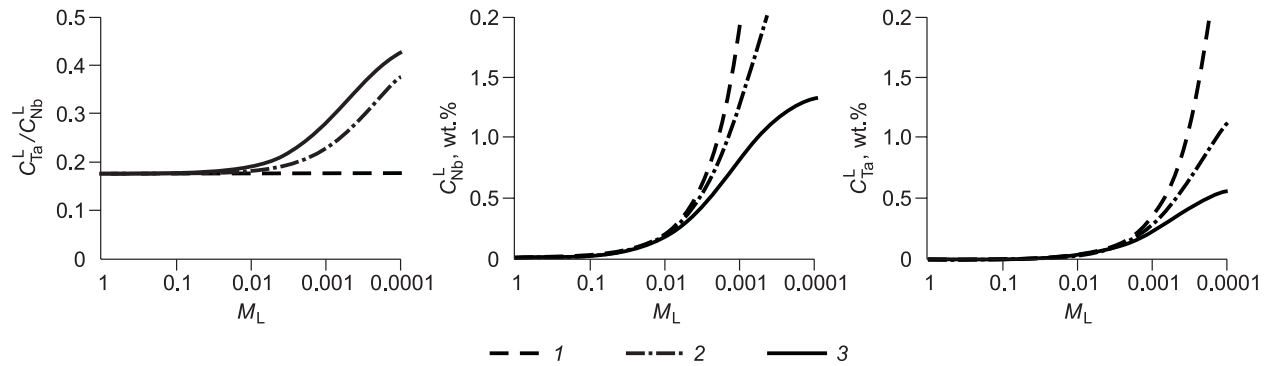


Fig. 3. Results of modeling in the system silicate melt–aqueous-fluid (L–fl). Changes in C_{Ta}^L/C_{Nb}^L and in the contents of Ta and Nb in the residual silicate melt: 1, ideal L–fl fractionation at $C_{H_2O}^{L(0)} = C_{H_2O}^{L(N)} = 15$ wt.% (coincides with the curve for a fluid-free system); 2, equilibrium system L–fl, in which the solubility of fluid increases from $C_{H_2O}^{L(0)} = 4$ to $C_{H_2O}^{L(N)} = 15$ wt.% (coincides with the curve for constant solubility, $C_{H_2O}^{L(0)} = C_{H_2O}^{L(N)} = 4$ wt.%); 3, equilibrium system L–fl at $C_{H_2O}^{L(0)} = C_{H_2O}^{L(N)} = 10$ wt.%.

The L–fl interaction within a closed system has the least effect on the change in C_{Ta}^L/C_{Nb}^L among all the considered processes (Table 1). As in case 1.1, the formation of fluid somewhat retards the accumulation of Ta and Nb in the residual silicate melt.

1.3. Silicate melt and liquid phase immiscible with it (L–B). Let us consider a system in which Ta and Nb are distributed between silicate (L) and aluminofluoride (LF) melts. The available factual material for this pair of phases permits us to assess the influence of the equilibrium on C_{Ta}^L/C_{Nb}^L . The K_{pMe} values and the compositions of equilibrium L and LF were earlier determined at 800 °C and 1 kbar (Gramenitskii and Shchekina, 1993; Gramenitskii et al., 2005; Alferyeva et al., 2011; Alferyeva, 2012).

In this system, fluorine serves as component Z marking the saturation of silicate melt with aluminofluoride melt (Gramenitskii et al., 2005). Therefore, formulas (7) for L–LF are written as

$$C_{Me}^{L(N)} = \frac{C_F^{LF(N)} C_{Me}^{L(N-1)} M_{L(N-1)}}{M_{L(N)} (C_F^{LF(N)} - K_{pMe} C_F^{L(N)}) + K_{pMe} C_F^{L(N)} M_{L(N-1)}}$$

or

$$C_{Me}^{L(N)} = \frac{C_F^{LF(1,2,\dots,N)} C_{Me}^{L_0}}{M_{L(N)} (C_F^{LF(1,2,\dots,N)} - K_{pMe} C_F^{L(N)}) + K_{pMe} C_F^{L_0}} \quad (10)$$

Under starting conditions, the concentration of F in granitic aluminosilicate melt L_0 is 0.2–0.3 wt.% (Badanina et al.,

Table 1. Results of calculation. C_{Ta}^L/C_{Nb}^L and contents of Ta and Nb in the residual silicate melt $M_L = 0.0001M_{L_0}$ in different model systems

Model system	C_{Ta}^L/C_{Nb}^L	C_{Ta}^L and C_{Nb}^L	
		wt. %	
L–S	0% Bt	0.18	19.9
	5% Bt	1.8–4.8	0.3
	20% Bt	>1900	1.5×10^{-6}
	5–0% Bt	0.2	12.8
	20–0% Bt	0.5–0.7	3.4
L–fl	15% fl (fractionation)	0.18	19.9
	4% fl (equilibrium)	0.37	3.0
	10% fl (equilibrium)	0.42	1.3
L–LF	LF (fractionation)	0.25	13.5
	LF (equilibrium)	0.7–0.9	0.7–0.8
L–TN A/NK = 1.3–1.7	$K_d = 1.7$	0.7	0.9*
	$K_d = 6.9$	2.9	2.1*

* The values correspond to the solubility product of columbite. For details, see section 2 (L–TN).

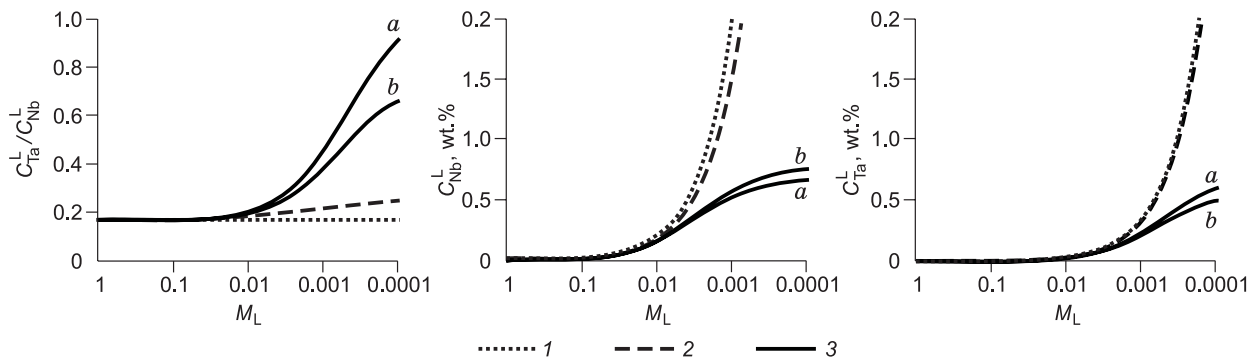


Fig. 4. Results of modeling in the system L–B by the example of interaction between silicate and aluminofluoride melts (L–LF). Changes in C_{Ta}^L/C_{Nb}^L and in the contents of Ta and Nb in the residual silicate melt: 1, LF does not form; 2, ideal L–LF fractionation; 3, equilibrium system L–LF. *a*, A/NK = 0.95; *b*, A/NK = 1.1.

2010). At 800 °C and 1 kbar, quartz-normative silicate melt can become saturated with aluminofluoride melt when it contains ≥ 5 wt.% F (Gramenitskii et al., 2005). In this case,

$$M_L / M_{L_0} = C_F^{L_0} / C_F^L = 0.04,$$

i.e., the saturation with LF can be reached at $\sim 96\%$ crystallization of the primary silicate melt.

According to (10) and earlier data (Gramenitskii et al., 2005; Alferyeva et al., 2011; Alferyeva, 2012) summarized in Table 2, the L–LF interaction can increase C_{Ta}^L/C_{Nb}^L in successively formed differentiates of silicate melt (Fig. 4). As in the system L–fl, the most considerable increase is observed under stable L–LF equilibrium and insignificant fractionation of these phases.

Aluminofluoride melt affects the distribution of metals stronger than an aqueous fluid. Even in the case of complete isolation of L and LF from each other, C_{Ta}^L/C_{Nb}^L in the silicate melt slightly increases at the late stage of differentiation. In a closed equilibrium system, the contents of metals in the silicate melt can become almost the same under L–LF interaction.

As in systems 1.1 and 1.2, the formation of LF affects negatively the accumulation of Ta and Nb in the residual silicate melt and leads to partial dispersion of these metals.

2. Silicate melt and isomorphous tantalite–columbite series (L–TN). Figure 5 shows the solubility products of minerals of the tantalite–columbite series in quartz-normative melts with different apfatic coefficients. The solubility of tantalite in all systems is slightly higher than the solubility of the extreme Nb end-member of columbite. There are little literature data on the solubility of Ta–Nb-columbites. The solubility product curve for the isomorphous columbite–tantalite series can be constructed only for the plumasite component of the system, based on the data of Chevychelov et al. (2010) and Aseri et al. (2015).

The solubility product of columbite in the plumasite component of the system is achieved when the content of crystalline substance in the system is about 99 wt.% (Fig. 6). The coefficients of Ta and Nb distribution (K_d) between the

melt and minerals of the columbite–tantalite series were obtained from experimental data (Chevychelov et al., 2010). For a medium-plumasite (A/NK = 1.3) system, $K_d = 1.7$, and for a high-plumasite (A/NK = 1.7) system, $K_d = 6.9$. The difference in the distribution coefficients leads to different values of C_{Ta}^L/C_{Nb}^L in the residual melt of different compositions (Fig. 6). The highest C_{Ta}^L/C_{Nb}^L ratio is observed in the high-plumasite system.

Thus, crystallization of minerals of the isomorphous columbite–tantalite series also increases C_{Ta}^L/C_{Nb}^L in the residual silicate melt. When crystallization of the system is accompanied by a significant fractionation of crystalline and

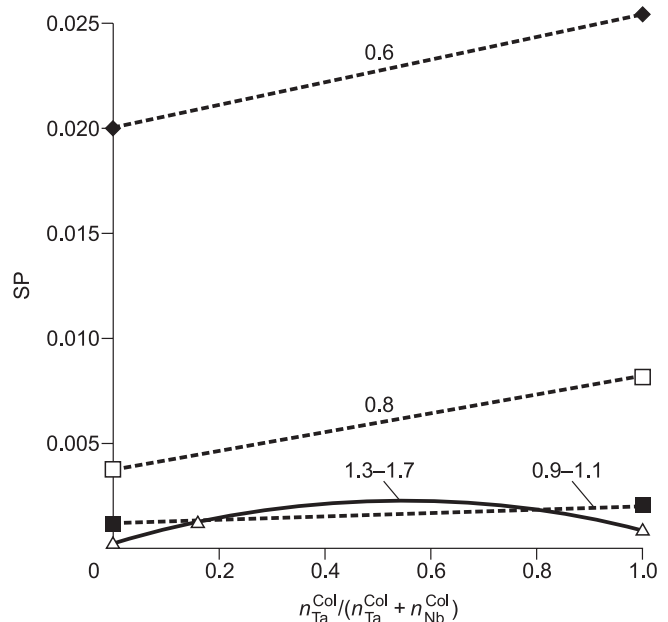


Fig. 5. Averaged solubility products of minerals of the isomorphous columbite–tantalite series (Linnen and Keppler, 1997; Chevychelov et al., 2010; Fiege et al., 2011; Aseri et al., 2015) depending on the molar Ta/Nb ratio ($n_{Ta}^{Col}/(n_{Ta}^{Col} + n_{Nb}^{Col})$). Dashed lines connect the SP values of the extreme end-members, obtained at the same A/NK values of the melt: 0.6, 0.8, or 0.9–1.1. Solid line is approximation of the SP values at A/NK = 1.3–1.7, expressed by the equation $y = -0.0066x^2 + 0.0072x + 0.0003$.

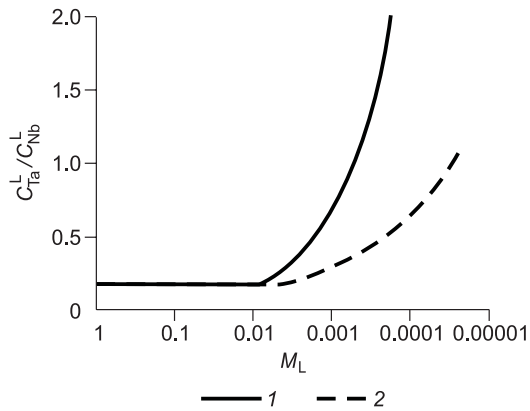


Fig. 6. Results of modeling in the system L–TN by the example of interaction between silicate melt and minerals of the isomorphous columbite–tantalite series. Changes in C_{Ta}^L/C_{Nb}^L in the residual silicate melt: 1, $K_d = 6.9$; 2, $K_d = 1.7$.

liquid phases and localization of the deeply differentiated residual melt, the achievement of the columbite–tantalite solubility product does not lead to significant dispersion of Ta and Nb.

The solubility product of columbite at the final stage of crystallization differentiation is determined by the C_{Ta}^L and C_{Nb}^L values equal to those at $M_L = 0.0001M_{L_0}$ of the system L–TN (Table 1).

Validity limits. All the above models are based on mass balance calculation only and do not reflect the course of crystallization depending on temperature, pressure, and fluid regime.

A change in K_d depending on the composition of the silicate melt and the contents of Mn and Fe in the system L–TN might contribute to the deviation from the above calculation. The solubility product values in the isomorphous columbite–tantalite series must be refined, because they are based on only one experimentally studied composition of Ta–Nb–columbite.

Under real conditions, C_{Ta}^L/C_{Nb}^L depends also on crystallization of pyrochlore, cassiterite, ilmenite, various dark-colored minerals, etc. The above calculation does not reflect the diversity of natural processes. It shows tendencies of changes in the above ratio and the relative intensity of the mechanisms of Ta and Nb distribution under interaction of the considered phases. Having the necessary empirical data and using the above formulas, it is possible to significantly expand the list of systems and, thus, to obtain a more

detailed pattern of Ta and Nb redistribution throughout the crystallization of the granite massif.

One of the promising phases that can participate in the formation of rare-metal deposits is a water–silicate liquid (WSL) (Smirnov et al., 2012, 2017; Thomas et al., 2014; Smirnov, 2015, 2017). It is included in none of the calculation models because of the scarce information about the conditions of its formation. This liquid can be regarded either as a phase formed in equilibrium with a silicate melt by the liquid immiscibility mechanism or as the silicate melt that has reached the corresponding composition through its gradual change. Having the necessary empirical data, it is possible to calculate the contribution of WSL (with due correction), using the L–B model in the first case and the L–TN model in the second.

For the same reason, pegmatites are not included into the list of natural objects in which the behavior of Ta and Nb can be calculated. Because of the diversity of the possible paths of evolution of pegmatite systems, the details of the formation of pegmatite melt are still ambiguous and can be considered special cases of the above-reported mechanisms.

Fractionation and magmatic differentiation. As the above calculation shows, crystallization of columbite can begin only when the content of crystalline substance in the system is ~99 wt.%. Formation of granite massifs with a high content of columbite–tantalite seems to be possible only under high fractionation of a crystalline metal-free material and a residual melt. At a first glance, such fractionation is doubtful in the case of viscous granite melts. However, some researchers (Dingwell et al., 1985, 1996; London, 2005; Giordano et al., 2008) report that an increase in the contents of water, fluorine, and alkaline metals in acid silicate melt leads to a significant decrease in its viscosity and its transformation into a specific fluidized melt. As a result, the most differentiated melt portions are more readily fractionate into a crystalline material and a liquid. In natural systems, a high degree of fractionation was established for albite–zinnwaldite microgranites of the Zinnwald deposit (Webster et al., 2004).

On the calculation, the starting contents of Ta and Nb in L_0 were specified at their Clarke values; in nature, barren parental granites of various deposits are analogs of such rocks. Based on the data of Beskin et al. (1994), it is possible to estimate the quantitative ratio of barren parent granites and their rare-metal differentiates by the example of the Khangilai pluton and the Orlovka Ta–Nb deposit in eastern Transbaikalia. According to the gravimetric-survey

Table 2. Contents of Ta and Nb (wt.%) in products of L and LF quenching (Gramenitskii et al., 2005; Alferyeva et al., 2011; Alferyeva, 2012)

No.	A/NK	Phase	Ta	Nb	K_{pTa}	K_{pNb}
1	0.95	L	1.6 ± 0.1	1.1 ± 0.1	0.12	0.73
		LF	0.2 ± 0.1	0.8 ± 0.3		
2	1.1	L	1.3 ± 0.1	1.1 ± 0.1	0.15	0.64
		LF	0.2 ± 0.1	0.7 ± 0.2		

data of the authors, the total volume of the parent granites of the Khangilai pluton can be estimated at $\sim 2500 \text{ km}^3$. The approximate volume of the ore-bearing granites of the deposit is no more than 0.6 km^3 , i.e., 0.02% of the total volume of the parent melt. Therefore, if the Orlovka massif is considered a product of crystallization differentiation of the Khangilai granite melt, then the crystallization of rare-metal granites of the deposit began when the content of crystalline material in the system was $\sim 99.98\%$. This value is a few fractions of a percent greater than the minimum degree of crystallization at the system mass balance, which is necessary for the beginning of columbite formation.

CONCLUSIONS

(1) Calculation of the mass balances using different experimental data has shown that all the described processes lead to an increase in Ta/Nb in the successively forming differentiates of granite melt.

(2) In contrast to the other described systems, the interaction of silicate melt and columbite–tantanite (L–TN) increases $C_{\text{Ta}}^{\text{L}}/C_{\text{Nb}}^{\text{L}}$ in the residual silicate melt and does not cause dispersion of Ta and Nb in the Earth's crust matter. Under ideal fractionation of the melt and crystalline phases throughout crystallization, the late saturation of the system with Col–Tan favors the formation of ore substance. The experimentally determined K_d and SP values ensure a significant increase in Ta/Nb, up to a predominance of Ta in deeply differentiated granite melts.

(3) Separation of an aqueous fluid from a magmatic melt in a closed system can lead to an increase in $C_{\text{Ta}}^{\text{L}}/C_{\text{Nb}}^{\text{L}}$, but the efficiency of the L–fl interaction is significantly lower than that in all the other considered systems.

(4) Aluminofluoride melt and dark-colored minerals play a similar role in the redistribution of Ta and Nb. Formation of these phases can lead to a significant increase in $C_{\text{Ta}}^{\text{L}}/C_{\text{Nb}}^{\text{L}}$ but also a considerable dispersion of metals in the Earth's crust matter and thus hinder the formation of Ta and Nb deposits.

We sincerely thank Yu.A. Stochkov, O.Yu. Lavrova, A.R. Kotelnikov, V.Yu. Chevychelov, P.Yu. Plechov, A.Yu. Bychkov, and D.Yu. Bychkov for interest to our research work and for fruitful discussion of its aspects.

This work was carried out the framework of the budget project “The regimes of petrogenesis of the inner geospheres”.

REFERENCES

- Acosta-Vigil, A., Buick, I., Hermann, J., Cesare, B., Rubatto, D., London, D., Morgan, G.B., 2010. Mechanisms of crustal anatexis: A geochemical study of partially melted metapelitic enclaves and host dacite, SE Spain. *J. Petrol.* 51, 785–821.
- Alferyeva, Ya.O., 2012. Silicate–Salt Liquid Immiscibility in the Model Granite and Nepheline–Syenite System Si–Al–Na–Li–H–F–O. PhD Thesis [in Russian]. Mosk. Gos. Univ., Moscow.
- Alferyeva, Ya.O., Gramenitskii, E.N., Shchekina, T.I., 2011. Experimental study of phase relations in a lithium-bearing fluorine-rich haplogranite and nepheline syenite system. *Int. Geochem.* 49 (7), 676–690.
- Alferyeva, Ya.O., Shchekina, T.I., Gramenitskii, E.N., 2018. Fluorine and water limits in highly evolved granite melts. *Vestnik Moskovskogo Universiteta. Ser. 4. Geologiya*, No. 3, 70–76.
- Ariskin, A.A., Barmina, G.S., 2000. Modeling of Phase Equilibria during Crystallization of Basaltic Magmas [in Russian]. MAIK “Nauka/Interperiodika”, Moscow.
- Aseri, A., Linnen, R., Xu Dong Che, Thibault, Y., Holtz, F., 2015. Effects of fluorine on the solubilities of Nb, Ta, Zr and Hf minerals in highly fluxed water-saturated haplogranitic melts. *Ore Geol. Rev.*, No. 64, 736–746.
- Badanina, E.V., Syritso, L.F., Volkova, E.V., Thomas, R., Trumbull, R.B., 2010. Composition of Li–F granite melt and its evolution during the formation of the ore-bearing Orlovka massif in eastern Transbaikalia. *Petrology* 18 (2), 131–157.
- Baker, D.R., Alletti, M., 2012. Fluid saturation and volatile partitioning between melts and hydrous fluids in crustal magmatic systems: The contribution of experimental measurements and solubility models. *Earth Sci. Rev.*, No. 114, 298–324.
- Beskin, S.M., 2014. Geology and Indicative Geochemistry of Ta–Nb Deposits in Russia (Rare-Metal Granites) [in Russian]. Nauchnyi Mir, Moscow.
- Beskin, S.M., Grebennikov, A.M., Matias, V.V., 1994. The Khangilai granite pluton and associated Orlovka Ta deposit in Transbaikalia. *Petrologiya* 2 (1), 68–87.
- Borodulin, G.P., Chevychelov, V.Yu., Zaraisky, G.P., 2009. Experimental study of partitioning of tantalum, niobium, manganese, and fluorine between aqueous fluoride fluid and granitic and alkaline melts. *Dokl. Earth Sci.* 427 (2), 868–873.
- Bowen, N.L., 1934. Evolution of Igneous Rocks [in Russian]. ONTI NKTP SSSR, Moscow.
- Chevychelov, V.Yu., Zaraisky, G.P., Borisovskii, S.E., Borkov, D.A., 2005. Effect of melt composition and temperature on the partitioning of Ta, Nb, Mn, and F between granitic (alkaline) melt and fluorine-bearing aqueous fluid: fractionation of Ta and Nb and conditions of ore formation in rare-metal granites. *Petrology* 13 (4), 305–321.
- Chevychelov, V.Yu., Borodulin, G.P., Zaraiskiy, G.P., 2010. Solubility of columbite, (Mn, Fe)(Nb, Ta)₂O₆, in granitoid and alkaline melts at 650–850 °C and 30–400 MPa: an experimental investigation. *Geochem. Int.* 48 (5), 456–464.
- Cerny, P., Ercit, T.S., 1985. Some recent advances in the mineralogy and geochemistry of Nb and Ta in rare-element granitic pegmatites. *Bull. Mineral.* 108, 499–532.
- Dingwell, D.B., Scare, C.M., Cronin, D.J., 1985. The effect of fluorine on viscosities in the system Na₂O–Al₂O₃–SiO₂: implications for phonolites, trachytes, rhyolites. *Am. Mineral.* 70, 80–87.
- Dingwell, D.B., Romano, C., Hess, K.-U., 1996. The effect of water on the viscosity of a haplogranitic melt under *P–T–X* conditions relevant to silicic volcanism. *Contrib. Mineral. Petrol.* 124, 19–28.
- Dolomanova, E.I., 1966. The probable role of liquation of silicate melts in ore formation, in: *Essays on the Geochemistry of Endogenous and Hypergene Processes* [in Russian]. Nauka, Moscow, 127–151.
- Fersman, A.E., 1960. Pegmatites [in Russian]. Izd. AN SSSR, Moscow.
- Fiege, A., Kirchner, C., Holtz, F., Linnen, R.L., Dziony, W., 2011. Influence of fluorine on the solubility of manganotantalite (MnTa₂O₆) and manganocolumbite (MnNb₂O₆) in granitic melts—An experimental study. *Lithos*, No. 122, 165–174.
- Forster, H.J., 1998. The chemical composition of REE–Y–Th–U-rich accessory minerals in peraluminous granites of the Erzgebirge–Fichtelgebirge region, Germany, Part I: The monazite-(Ce)-brabantite solid solution series. *Am. Mineral.* 83, 259–272.
- Giordano, D., Russell, J.K., Dingwell, D.B., 2008. Viscosity of magmatic liquids: A model. *Earth Planet. Sci. Lett.*, No. 271, 123–134.

- Gramenitskii, E.N., Shchekina, T.I., 1993. Phase relations in the liquidus part of the fluorine-containing granite system. *Geokhimiya*, No. 6, 821–840.
- Gramenitskii, E.N., Shchekina, T.I., Devyatova, V.N., 2005. Phase Relations in Fluorine-Containing Granite and Nepheline–Syenite Systems and Distribution of Elements between the Phases [in Russian]. GEOS, Moscow.
- Haapala, I., 1997. Magmatic and postmagmatic processes in tin-mineralized granites: topaz-bearing leucogranite in the Eurajoki rapakivi granite stock, Finland. *J. Petrol.* 38 (12), 1645–1659.
- Haapala, I., Lukkari, S., 2005. Petrological and geochemical evolution of the Kymi stock, a topaz granite cupola within the Wiborg rapakivi batholith, Finland. *Lithos* 80, 347–362.
- Holtz, F., Dingwell, D.B., Behrens, H., 1993. Effects of F, B₂O and P₂O₅ on the solubility of water in haplogranite melts compared to natural silicate melts. *Contrib. Mineral. Petrol.* 113, 492–501.
- Kogarko, L.N., Krigman, L.D., 1981. Fluorine in Silicate Melts and Magmas [in Russian]. Nauka, Moscow.
- Kovalenko, V.I., 1977. Petrology and Geochemistry of Rare-Metal Granitoids [in Russian]. Nauka, Novosibirsk.
- Lenharo, S., Pollard, P.J., Helmut, B., 2003. Petrology and textural evolution of granites associated with tin and rare-metals mineralization at the Pitinga mine, Amazonas, Brazil. *Lithos* 66, 37–61.
- Linnen, R.L., Keppler, H., 1997. Columbite solubility in granitic melts: consequences for the enrichment and fractionation of Nb and Ta in the Earth's crust. *Contrib. Mineral. Petrol.* 128, 213–227.
- London, D., 2005. Granitic pegmatites: an assessment of current concepts and directions for the future. *Lithos* 80, 281–303.
- Maaloe, S., 1976. Quantitative aspects of fractional crystallization of major elements. *J. Geol.* 84, 81–96.
- Nash, W., Crecraft, H., 1985. Partition coefficients for trace elements in silicic magmas. *Geochim. Cosmochim. Acta* 49, 2309–2322.
- Peretyazhko, I.S., Savina, E.A., 2010. Fluid and magmatic processes in the formation of the Ary-Bulak ongonite massif (eastern Transbaikalia). *Russian Geology and Geophysics (Geologiya i Geofizika)* 51 (10), 1110–1125 (1423–1442).
- Peretyazhko, I.S., Savina, E.A., Dril', S.I., Gerasimov, N.S., 2011. Rb–Sr isotope system and Rb–Sr partitioning in the rocks of the Ary-Bulak ongonite massif, formed with the participation of fluoride–silicate magmatic immiscibility. *Russian Geology and Geophysics (Geologiya i Geofizika)* 52 (11), 1401–1411 (1776–1789).
- Reif, F.G., 2009. Conditions and Mechanisms of Formation of Ore-Magmatic Granite Systems (from Data of Fluid Inclusion Studies): Selected Scientific Works [in Russian]. IMGRE, Moscow.
- Ryabchikov, I.D., Hamilton, D.L., 1971. The possibility of separation of concentrated chloride solutions during crystallization of acid magmas. *Dokl. Akad. Nauk SSSR* 197 (4), 933–936.
- Shchekina, T.I., Gramenitskiy, E.N., Alferyeva, Ya.O., 2013. Leucocratic magmatic melts with the maximum fluorine concentrations: experiment and relations in nature. *Petrology* 21 (5), 454–470.
- Smirnov, S.Z., 2015. The fluid regime of crystallization of water-saturated granitic and pegmatitic magmas: a physicochemical analysis. *Russian Geology and Geophysics (Geologiya i Geofizika)* 56 (9), 1292–1307 (1643–1663).
- Smirnov, S.Z., Thomas, V.G., Kamenetsky, V.S., Kozmenko, O.A., Large, R.R., 2012. Hydrosilicate liquids in the system Na₂O–SiO₂–H₂O with NaF, NaCl and Ta: evaluation of their role in ore and mineral formation at high *T* and *P*. *Petrology* 20 (3), 271–285.
- Smirnov, S.Z., Thomas, V.G., Kamenetsky, V.S., Kozmenko, O.A., 2017. Hydrosilicate liquids in the system rare-metal granite–Na₂O–SiO₂–H₂O as accumulators of ore components at high pressure and temperature. *Petrology* 25 (6), 625–635.
- Solodov, N.A., 1978. Problems of Geochemistry of Trace Elements [in Russian]. Nauka, Moscow.
- Solovov, A.P. (Ed.), 1990. Geochemical Search for Minerals: A Reference-Book [in Russian]. Nedra, Moscow.
- Syritsko, L.F., Tabuns, E.V., Volkova, E.V., Badanina, E.V., Vysotskii, Yu.A., 2001. Model for the genesis of Li–F granites in the Orlovka massif, eastern Transbaikalia. *Petrology* 9 (3), 268–290.
- Tauson, L.V., 1977. Geochemical Types and Ore Potential of Granitoids [in Russian]. Nauka, Moscow.
- Thomas, V.G., Smirnov, S.Z., Kozmenko, O.A., Drebuschak, V.A., Kamenetsky, V.S., 2014. Formation and properties of hydrosilicate liquids in the systems Na₂O–Al₂O₃–SiO₂–H₂O and granite–Na₂O–SiO₂–H₂O at 600 °C and 1.5 kbar. *Petrology* 22 (3), 293–309.
- Valyashko, V.M., 1990. Phase Equilibria and Properties of Hydrothermal Systems [in Russian]. Nauka, Moscow.
- Veksler, I.V., 2004. Liquid immiscibility and its role at the magmatic-hydrothermal transition: a summary of experimental studies. *Chem. Geol.* 210 (1–4), 7–31.
- Webster, J., Thomas, R., Forster, H.J., Seltmann, R., Tappen, Ch., 2004. Geochemical evolution of halogen-enriched granite magmas and mineralizing fluids of the Zinnwald tin–tungsten mining district, Erzgebirge, Germany. *Mineral. Deposita* 39, 452–472.
- Zaraisky, G.P., Aksyuk, A.M., Devyatova, V.N., Udoratina, O.V., Chevychelov, V.Yu., 2009. The Zr/Hf ratio as a fractionation indicator of rare-metal granites. *Petrology* 17 (1), 25–45.

Editorial responsibility: Yu.N. Pal'yanov